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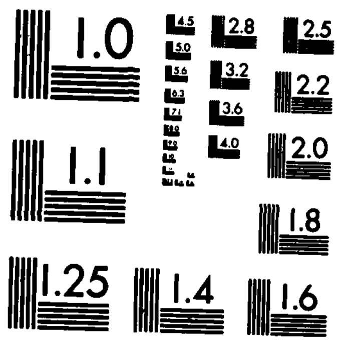

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Quantum Dynamical Model for Laser Excitation of a Two-Level Adatom: Surface-Dressed Bloch Equations

by

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Quantum Dynamical Model for Laser Excitation of a Two-Level Adatom: Surface-Dressed Bloch Equations

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Abstract

Surface-dressed Bloch equations are derived from a microscopic Hamiltonian which includes the interactions among an adatom, the laser photon and the phonon modes. The influence of the surface on the population inversion of the adatom is analyzed in terms of: (i) the reflected-field-induced damping factor which depends on the orientation of the transition dipole and the adatom-surface separation and (ii) the frequency shift and damping factor induced by the phonon modes.

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I. Introduction

The interaction of laser radiation with matter in homogeneous systems has been extensively studied for the past several years.[1,2] However, for heterogeneous systems (e.g., gaseous atoms near or adsorbed on a solid surface) the laser-stimulated surface phenomena (desorption, dissociation, migration and reactions) involving both multiphoton and multiphonon processes have been only recently attacked.[3-5] In previous studies, we have investigated the excitation and relaxation dynamics of adspecies subjected to IR radiation in which only the vibrational degrees of freedom are concerned.[4] In the present paper, we shall investigate the electronic excitation of a two-level atom adsorbed on a metal surface and subjected to UV or visible laser radiation. In the absence of a solid surface or when the atom is very far from the surface, the population inversion and the power spectrum of the system may be described by an ordinary optical Bloch equation (OBE). In the presence of a surface at a distance from the adatom which is comparable to the optical wavelength, the dynamical phenomena are influenced by the following factors: (i) nonradiative energy relaxation of the excited atom via electron-phonon coupling; (ii) radiative spontaneous decay and stimulated emission produced by both the applied field and the reflected field; (iii) the oscillatory behavior of the lifetime of the adatom due to the interference between the applied field and the reflected field; (iv) the reflectivity and refraction index of the surface; (v) surface-induced dephasing of the dipole; and (vi) interaction between the adatom and plasmons; as a first step, we assume that the effects of the conduction electrons in the metal just provide a reflected field acting back to the adatom.

II. Microscopic Hamiltonian and Surface-Dressed Bloch Equations

To investigate the above surface phenomena, we start with a microscopic Hamiltonian describing a two-level adatom subjected to laser radiation,

$$H = H_A + H_B + H_F + H_{AB} + H_{AF} + H_{AR} + H_{BF}. \tag{1}$$

H_A, H_B and H_F are the unperturbed Hamiltonians for the adatom, phonon and photon (laser) modes, respectively; H_{AB}, H_{AF} and H_{AR} describe the interaction of the adatom (A) with the phonon bath (B) modes, the applied field photon (F) modes and the reflected field (R), respectively; and H_{BF} is the interaction between the B modes and the applied field. For a laser frequency in the visible to UV range, the phonon (B) modes have much weaker absorption compared to that of the adatom, and thereby the direct heating of the substrate due to H_{BF} is negligible. In this work, the effect of H_{BF} will be displayed in terms of the strength of the reflected electric field due to the reflectivity of the surface.

Employing Pauli's matrices for the two-level adatom and harmonic ladder operators for the photon and phonon modes, the total Hamiltonian may be expressed in a second-quantization form which leads to the equations of motion, in the rotating-wave approximation, as follows:[4]

$$\dot{\sigma}_{12} = -i\omega_0\sigma_{12} + i\sum_{\nu} G_\nu B_\nu \sigma_3 + i\sum_{\lambda} C_\lambda a_\lambda \sigma_3 - \gamma_R \sigma_{12} \quad , \tag{2a}$$

$$\dot{\sigma}_3 = 2i\sum_{\lambda} C_\lambda (a_\lambda^\dagger \sigma_{12} + a_\lambda \sigma_{21}) + 2i\sum_{\nu} G_\nu (B_\nu^\dagger \sigma_{12} + B_\nu \sigma_{21}) \quad , \tag{2b}$$

$$\dot{a}_\lambda = -i\omega a_\lambda + iC_\lambda \sigma_{12} \quad , \tag{2c}$$

$$\dot{B}_\nu = -i\bar{\omega}_\nu B_\nu - i\sum_{\nu} G_\nu N_\nu \sigma_{12} \quad . \tag{2d}$$

$\sigma_{ij} = |i\rangle\langle j|$ is the atomic transition operator, $\sigma_3 = \sigma_{22} - \sigma_{11}$, and ω_0 and ω are the adatomic transition and laser field frequencies, respectively; C_λ and G_ν are the coupling coefficients in the interaction Hamiltonians H_{AF} and H_{AB}, respectively; the multi-phonon processes are governed by the phonon operator, B_ν, frequency, $\bar{\omega}_\nu$, and occupation number, N_ν, given by[5]

$$B_\nu = \prod_j^{\nu} b_j , \quad \bar{\omega}_\nu = \sum_j^{\nu} \omega_j \quad , \tag{3a}$$

$$N_\nu(T) = \prod_j (\bar{n}_j + 1) - \prod_j \bar{n}_j \quad , \tag{3b}$$

$$\bar{n}_j(T) = (e^{\hbar\omega_j/kT} - 1)^{-1} \quad , \tag{3c}$$

where ω_j is the frequency of the j-th phonon mode with a thermal equilibrium occupation number at temperature T defined by Eq. (3c). The applied laser field is quantized by its ladder operator a_λ for the λ-th mode.

The effects of the quantized reflected field come in through the last term in Eq. (2a), which depends on the damping factor γ_R,

$$\gamma_R = 2|\mu_{12}|^2 \mathit{Im} f/\hbar \ , \tag{4}$$

where μ_{12} is the electric-dipole transition matrix element between states $|i\rangle$ and $|j\rangle$. The function $f(d) \equiv \mathit{Re} f(d) + i\mathit{Im} f(d)$, depending on the orientation of the dipole with respect to the surface, is given by[6]

$$f_\perp(d) = -R\left(\frac{2}{\bar{\lambda}^3}\right)\left[\left(\frac{1}{(2\hat{d})^3} - \frac{i}{(2\hat{d})^2}\right)e^{2i\hat{d}}\right] \tag{5a}$$

$$f_\parallel(d) = R\left(\frac{1}{\bar{\lambda}^3}\right)\left[\left(\frac{1}{(2\hat{d})^3} + \frac{1}{2\hat{d}} - \frac{i}{(2\hat{d})^2}\right)e^{2i\hat{d}}\right] \tag{5b}$$

for the perpendicular and parallel cases. The reduced distance is $\hat{d} = d/\bar{\lambda} = 2\pi d/\lambda$, where d is the distance of the adatom from the surface and λ is the wavelength of the field. R is the reflectivity of the surface taking into account the interaction between the phonon modes and the field, H_{BF}. Since $R \approx 1$, we shall neglect the effects of H_{BF} and assume a perfectly reflective surface.

With the help of many-body techniques applied to multiphonon processes,[5,7] we obtain the surface-dressed Bloch equations (SBE):[8]

$$\frac{d}{dt}\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} -\tilde{\gamma}_2 & -\tilde{\Delta} & 0 \\ \tilde{\Delta} & -\tilde{\gamma}_2 & \Omega \\ 0 & -\Omega & -\tilde{\gamma}_1 \end{pmatrix}\begin{pmatrix} u \\ v \\ w \end{pmatrix} + \tilde{\gamma}_1\begin{pmatrix} 0 \\ 0 \\ w_{eq} \end{pmatrix} . \tag{6}$$

u and v are the components, in units of the transition moment, of the adatomic dipole moment "in phase" and "in quadrature" with the applied field. w is the population inversion, $w \equiv \langle\sigma_3\rangle$, with the equilibrium value w_{eq}, where $w_{eq} = -1$ for the adatom initially in its ground state and $w_{eq} = 1$ for the excited state. $\Omega = |\mu_{12}E_0|/\hbar$ is the Rabi frequency and is proportional to the amplitude of the applied electric field, E_0, which is assumed to have a slowly-varying envelope. $\tilde{\gamma}_1$ and $\tilde{\gamma}_2$ are the relaxation factors for the inversion and for the dipole, respectively, and $\tilde{\Delta}$ is the effective detuning of the laser field frequency with respect to the adatomic transition frequency. These surface-dressed parameters are related to the surface-free parameters by

$$\tilde{\Delta} = \Delta + \delta\omega_F + \delta\omega_B \quad , \tag{7a}$$

$$\tilde{\gamma}_1 = 2(\gamma_B + A/2) \quad , \tag{7b}$$

$$\tilde{\gamma}_2 = \gamma_B + A/2 + \gamma_2 + \gamma_R \quad , \tag{7c}$$

where $\Delta = \omega_0 - \omega$ is the surface-free detuning, A is the Einstein coefficient for spontaneous emission, $\delta\omega_F$ and $\delta\omega_B$ are the frequency shifts due to the applied field and phonons, respectively, and γ_B and γ_2 are the phonon-induced energy (T_1) and phase (T_2) relaxation rates, respectively. The phonon-induced frequency shift and damping factor are given by[5]

$$\delta\omega_B = P\sum_\nu \frac{|G_\nu|^2 N_\nu}{\omega_0 - \bar{\omega}_\nu} , \quad P \equiv \text{principal part} \tag{8a}$$

$$\gamma_B = \sum_\nu |G_\nu|^2 N_\nu \, \delta(\omega_0 - \bar{\omega}_\nu) \tag{8b}$$

which, in contrast to that of the optically-induced parameters, are strongly temperature dependent through the multiphonon occupation number, $N_\nu(T)$, given by Eq. (3b). We note that these features of temperature dependence disappear when just a single-phonon process is considered in H_{AB}.

The steady-state population inversion is found analytically to be (for $w_{eq} = -1$)

$$w_{s.s.} = \left(1 + \frac{(\tilde{\gamma}_2/\tilde{\gamma}_1)\Omega^2}{\tilde{\Delta}^2 + \tilde{\gamma}_2^2}\right)^{-1} , \tag{9}$$

which is sensitive to the reduced distance and dipole orientation through the surface-dressed parameters $\tilde{\gamma}_1$, $\tilde{\gamma}_2$ and $\tilde{\Delta}$. We see from the above equation that the criterion for the weak-field limit in the SBE, given by

$$\Omega^2 << (\tilde{\Delta}^2 + \tilde{\gamma}_2^2)\tilde{\gamma}_1/\tilde{\gamma}_2 \quad ,$$

is a weaker condition than that in the surface-free OBE due to the surface-dressed parameters.

III. Discussion

The SBE displayed in Eq. (6) are different from the surface-free OBE due to the influence of the reflected field, γ_R, and the effects of the electron-phonon coupling, $\delta\omega_B$ and γ_B. We note that these surface-induced effects are characterized by various system parameters such as the temperature of the surface, the orientation and position of the induced dipole of the adatom, the transition frequencies of the adatom (ω_0) and the phonons (ω_j), and the wave-length of the applied field. For example, by the concept of the "energy gap law", $\delta\omega_B$ and γ_B increase when the temperature of the surface increases and/or the order of the multiphonon coupling, p, defined by $p \equiv (\omega_B + \delta\omega_A + \delta\omega_B)/\omega_j$ where $\delta\omega_A$ is the frequency shift due to the multimode property of the laser, decreases.[4,5] From Eqs. (4) and (5), we see that γ_B is sensitive to the reduced distance, $d = d/2\pi\lambda$, where for sufficiently small $\hat{d}$ the value of γ_B oscillates as a function of d, as does also the lifetime of the adatom.

In conclusion, we have shown that from a microscopic Hamiltonian the SBE can be obtained, which exhibit important surface effects on the excitation of a two-level atom. The results suggest that monochromatic laser radiation might be used not only as a characterization of surface adspecies, such as orientation, but also as a probe of the dynamics of rate processes occurring at a solid surface both for vibrational and electronic excitations.

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